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"FUNDAMENTAL STUDY OF DENSE-FLUID DETONATION"

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SUMMARY

(1) TECHNICAL PROBLEM

We are investigating mathematical models of detonation in dense fluids and in solids. We wish to obtain a fundamental understanding of the interaction of pressure waves, or shockwaves, with high explosives.

(2) GENERAL METHODOLOGY

We are solving the steady-state dynamical equations of continuum mechanics, including viscosity, conductivity, and chemical reactions, to simulate detonation in fluids capable of undergoing fast exothermic reactions. We are solving the coupled ordinary differential equations of motion of molecular dynamics, for solids, to simulate the initiation process preceding detonation. We are examining simple models designed to describe the results of these macroscopic and microscopic approaches.

(3) TECHNICAL RESULTS

We have obtained detonation wave profiles, using a realistic dense-fluid equation of state. We have compared these profiles to the predictions of the simplified Zeldovich-Von Neumann-Doering model.

We have developed methods for simulating the rapid uniaxial compression of solids suited to molecular dynamics simulation.

We have formulated the interatomic distribution function in solids, for comparison with atomistic simulations and use in kinetic reaction models.

(4) IMPLICATION FOR FURTHER RESEARCH

The relatively long vibrational relaxation times occurring in shocked diatomic molecules with realistic values of viscosity and thermal conductivity

suggest that the nonequilibrium distribution of energy is more important than the interaction of ordinary transport properties with chemical reactions. We therefore intend to concentrate, in the next two years, on reaction initiation and intramolecular energy transfers in reacting molecules in the solid phase.

I. INTRODUCTION

Shock and detonation waves involve atomic-scale processes which are imperfectly understood and hard to measure. For this reason we have embarked on a program, using modern computational methods, of studying the processes through which mechanical shockwave energy stimulates the release of chemical energy within a detonation wave.

Our work entails the correlation of two points of view: continuum mechanics and atomic mechanics. We seek to understand the limitations of the continuum approach in dealing with atomic-scale problems and to develop methods for describing these small-scale processes in a realistic way.

Considerable information on the equilibrium and transport properties of simple systems is now available(1,2). Computer simulations of dense fluids, coupled with thermodynamic perturbation theories(3) based on simple hard and soft sphere models, make it possible to describe the pressure-volume-temperature equation of state accurately, for sufficiently simple materials. For some "realistic" potentials, such as the Lennard-Jones 6-12 interatomic potential, comprehensive computer simulation studies have established the density and temperature dependence of the viscosities and the thermal conductivity as well(2). Much less is known about the contribution of intramolecular degrees of freedom to the transport properties and equation of state. Studies on molecules like methane and benzene indicate that the computer simulation approach is now feasible, even for molecules containing several atoms(4).

A numerical study, comparing the continuum and atomistic versions of a very strong dense-fluid shockwave made use of both the equilibrium and non-equilibrium constitutive properties of the 6-12 potential, and indicated that useful conclusions could be drawn by comparing the two approaches(5). A natural extension of that work is to consider the possibility of coupling

chemical reactions with the dissipative processes of viscosity and thermal conductivity which appear in shockwaves. That coupled combination is a detonation wave.

The simplest prototype condensed-phase high explosive is probably nitric oxide, NO. This molecule forms molecular nitrogen and oxygen in an exothermic reaction generating approximately 100 kilobars pressure(6). We set out with the goal of simulating the detonation of liquid NO using both the continuum and atomistic approaches. The continuum calculations are complete. Using an equation of state which describes the Lennard-Jones potential throughout the fluid regions of the phase diagram, and transport coefficients from the Enskog theory, we have generated detonation profiles as functions of the energy release and activation energy of the dense-fluid detonation. These calculations, including viscosities and thermal conductivity, are compared to the Zeldovich-Von Neumann-Doering model in Section II.

Shortly after this work was begun, a research program was initiated at Los Alamos, designed to measure and to model the detonation of nitric oxide. This program includes experimental, quantum mechanical, and dynamical groups working toward a common goal. Related Los Alamos research, carried out by Brad Holian, Galen Straub, and their co-workers, has established that the equilibration time between vibrational and translational temperatures in dense diatomic fluids (nitrogen) is relatively long(7), just as in the gas phase. These long equilibration times, of order 100 vibration times, suggest that the complete combustion process is impractically long for an atomistic simulation. For this reason we have concentrated our more recent work on solid-phase initiation and mode equilibrium. We are developing solid-phase calculations in which chemically active molecules can be studied under uniaxial and homogeneous

adiabatic compression. That work is described in Sections III and IV. We expect to devote the next two years' effort to enhancing our understanding of solid-phase detonation initiation from the atomistic mechanical point of view.

II. DENSE-FLUID DETONATION WAVE STRUCTURE

The classical steady one-dimensional ZND (for Zeldovich, Von Neumann, and Doering) model of detonation-wave structure can be summarized with the help of Figure 1. It is assumed that the reactants can assume the equilibrium unreacted thermodynamic states shown on the lower Hugoniot curve as the result of shock compression. Each of these states satisfies the condition that its mass, momentum, and energy fluxes agree with those characterizing the initial state (state 0). This unreacted Hugoniot is hypothetical because chemical reactions will gradually transform the reactants, at least for strong enough shockwaves, to hot products.

The fully reacted products can also be described by a Hugoniot curve satisfying the conservation laws. This is the upper Hugoniot. Its position, relative to the lower Hugoniot, depends upon the heat of reaction Q. The Zeldovich-Von Neumann-Doering detonation wave model pictures the detonation process as two consecutive steps: first, the reactants are shock-compressed to the (Von Neumann spike) state S. Next, these hot reactants slowly undergo chemical reactions, proceeding to the final (Chapman-Jouguet) state CJ. During the reaction phase the state point follows the Rayleigh line, satisfying the constraints of constant mass and momentum flux necessary in a steady wave. Neither the transport coefficients nor the reaction rate enter into Figure 1. These state functions determine the space and time scales associated with the compression and reaction phases of the detonation wave.

The ZND model is an oversimplification. With the theory of liquids sufficiently advanced that quantitative calculations, including nonideal effects, can be made, there is no real need for an inaccurate treatment.

Molecular dynamics simulations have shown that strong dense-fluid shockwaves can be described fairly well by the Navier-Stokes equation(5). Figure 2

indicates the relatively good agreement between the Navier-Stokes continuum calculations and the atomistic simulations. The principle disagreements are these: The wave is about 30% broader than the continuum predictions and the velocity distribution is considerably more complex than is the equilibrium Maxwell-Boltzmann distribution. The alternative Mott-Smith approach(8), in which the velocity distribution is a weighted average of the reactant and product Maxwellian distributions, grossly overestimates the nonequilibrium character of the wave.

We initially planned to carry out a similar comparison for nitric oxide, a simple liquid which undergoes the reaction

$$2NO = N_2 + O_2. \qquad (1)$$

Exploratory calculations fitted to the kinetics of the reaction showed that the reaction zone extends for thousands of angstroms, far too long for molecular dynamics simulation. The liquid detonation wave profile that we display in Figure 3, together with the ZND approximation to that profile, was calculated(9) with an activation energy approximately half that of nitric oxide. This substantially reduced the spatial extent of the detonation wave. Under this artificial assumption there is a noticeable quantitative discrepancy between the simple two-step model and the solution of the coupled equations. There is no such dramatic difference for nitric oxide, at least for a one-dimensional wave.

The instability of one-dimensional low-density detonation waves is well-established experimentally(10). Because this effect is at least as important as that of the hydrodynamic transport coefficients we see that further study of the one-dimensional detonation wave for nitric oxide, is not feasible, using molecular dynamics.

Vibrational energy transfer is very slow in diatomic molecules because the single vibrational mode is well-separated from the "lattice modes." The situation is less clear cut for polyatomic molecules with many degrees of freedom. Can the solid-phase initiation problem be understood using equilibrium chemical kinetics and equilibrium energy surfaces? Are nonequilibrium velocity distributions and intramolecular energy transfer significant? The answers to these questions are unknown despite considerable interest and debate(11). We are concentrating our efforts on enhanced understanding of solid-phase initiation, using the methods outlined in the following sections.

III. COMPUTER SIMULATIONS AT HIGH RATES OF STRAIN

To explore the rapid deformation associated with shockwaves in condensed fluids and solids we have developed special methods for solving the equations of motion of atoms in a rapidly-deforming fluid or solid(12). These methods were originally developed and applied to the simulation of viscous flows(13) and were later applied to solid-phase plasticity(14). In either case the macroscopic flow is described by a given strain-rate tensor ∇u, where u is the hydrodynamic flow velocity. To incorporate the flow velocity into the equations of motion, a perturbation, the tensor product of ∇u and Doll's tensor (the dyadic composed the particles' summed coordinate-momentum product qp) is added to the Hamiltonian function. Equations of motion result which include contributions proportional to the strain rate:

$$\begin{aligned} \dot{q} &= (p/m) + q\cdot\nabla u \ ; \\ \dot{p} &= F - \nabla u\cdot p \ ; \\ \dot{E} &= - VP:\nabla u \ . \end{aligned} \qquad (2)$$

Equations (2) describe adiabatic homogeneous deformation. This scheme has been used to make quantitative estimates of the shear and bulk viscosities for dense fluids.

Inhomogeneous compressions must be treated differently. The system is sheared or compressed by moving periodic images(5). Either method could be applied to chemically-reacting solids. We expect to explore the homogeneous uniaxial compression of two systems: The simple reaction model described in the next section and a "realistic" three-dimensional polyatomic model of a detonating solid. This latter application should allow us to map out the path followed by energy during the equilibration process.

IV. ATOMIC DISTRIBUTION FUNCTIONS IN SOLIDS

We are currently investigating a simple model for reacting atoms: Two atoms sufficiently close together react, releasing an energy Q. Equilibrium simulations (with Q=0) have been carried out to determine the density, strain, and temperature dependence of the "reaction rate." Figure 4 indicates the substantial dependence on strain biaxiality. Pastine's model(15), which contains an adjustable collision frequency ω, can be used to fit the uniaxial compression results.

A more fundamental approach incorporates the distribution of neighboring atoms. In the quasiharmonic case this can be done exactly. We have developed a numerical method for the partial integration of the Boltzmann factor, $\exp(-\Phi/kT)$, over all but two particle coordinates, leading to an atom-atom distribution function. This function is a product of Gaussians.

Because the calculation is somewhat intricate it is important to have a check available. The close-packed lattice, with nearest-neighbor interactions, is ideal for this purpose. Because the potential energy of a nearest-neighbor pair in a D-dimensional close-packed crystal is $kT/(D+1)$, the mean-squared deviation in the nearest-neighbor spacing should be $2kT/(D+1)\kappa$, where κ is the nearest-neighbor force constant. We have verified that this result is reproduced exactly by our numerical approach, and find that the convergence of higher-order and transverse correlations is relatively rapid and smooth as the number of particles in the periodic cell is increased. In the two-dimensional case, for example, the ratios of the nearest-neighbor mean-squared longitudinal to transverse fluctuations for 9, 16, 25, and 36-atom crystals are 0.667, 0.688, 0.695, and 0.696(16).

We expect to apply this same technique to the atom-atom distribution function for polyatomic crystals undergoing uniaxial compression. This analog of Pastine's model should prove useful in estimating the dependence of reaction rate on the macroscopic strain rate.

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FIGURES:

1. Diatomic reactant and product Hugoniots calculated with the Lennard-Jones equation of state. The well depth and collision diameter are ε and σ, respectively. The initial volume is $0.8442N\sigma^3$. The initial temperature is $0.722\varepsilon/k$.
2. Shockwave profile for a strong fluid shock carrying the triple-point argon to a final temperature of about one electron volt. The smooth curves are the Navier-Stokes solution. The points correspond to data from nonequilibrium molecular dynamics.
3. Detonation profile calculated using (a) the hydrodynamic equations, including viscosity and heat conduction, and (b) using the ZND model. The activation energy is artifically reduced to enhance the difference between the two approaches. The heat of reaction is 100ε and the activation energy is 70ε.
4. Reaction rate as a function of density for a simple binary-collision model. Both uniaxial and hydrostatic compressions are shown at a temperature about half the melting temperature. Pastine's model for the rate is shown as the full curve.

Figure 1

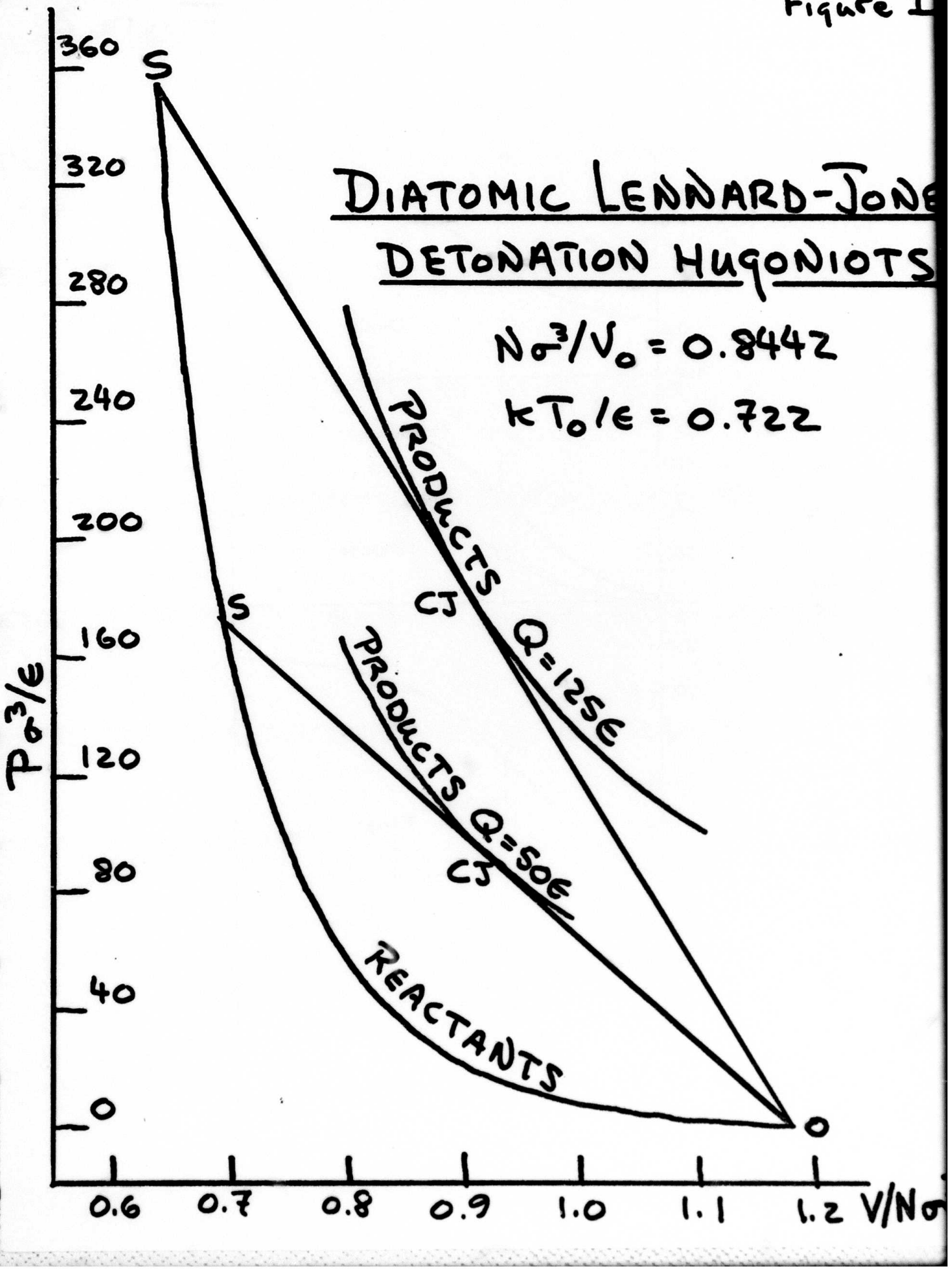
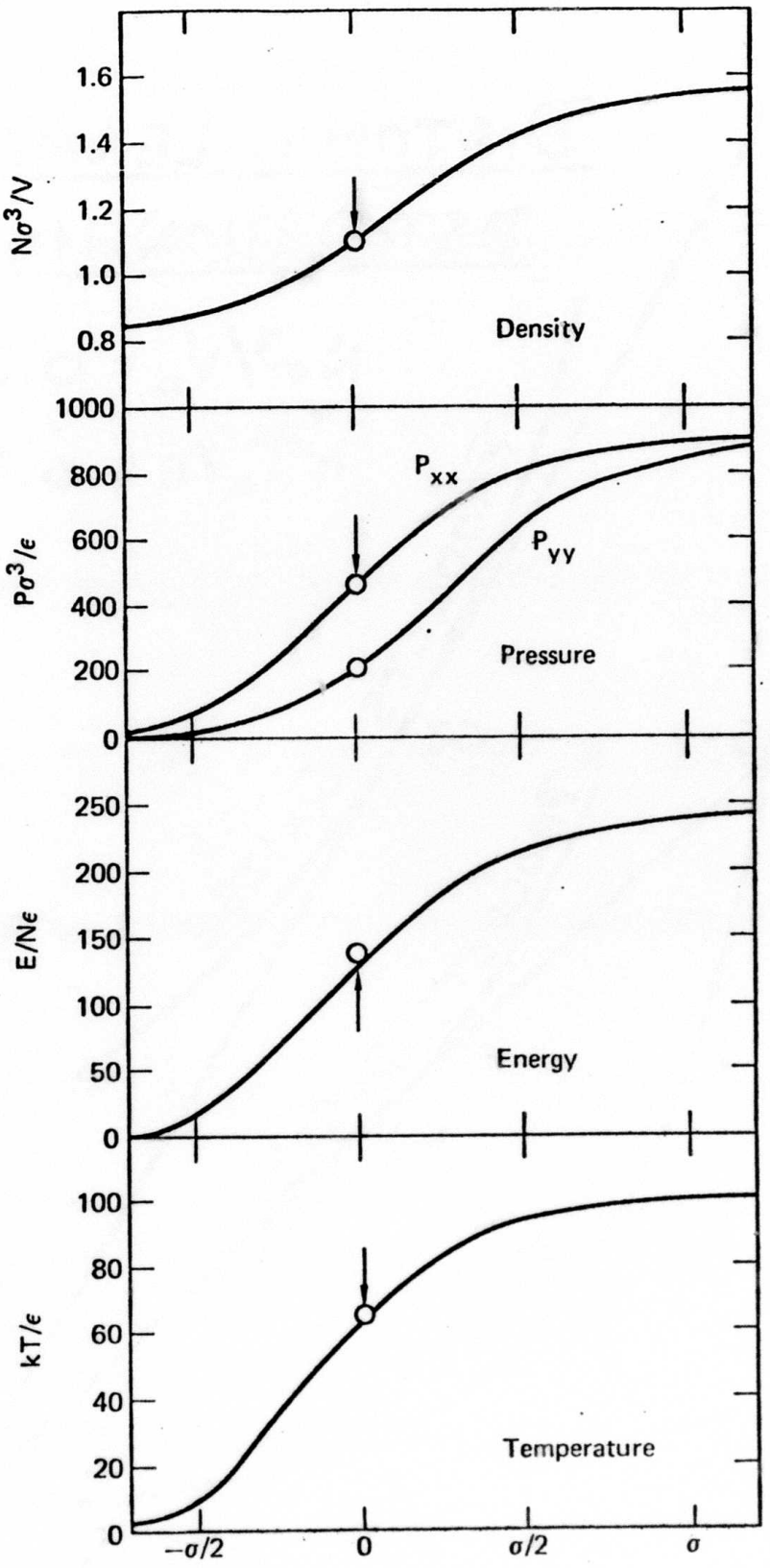
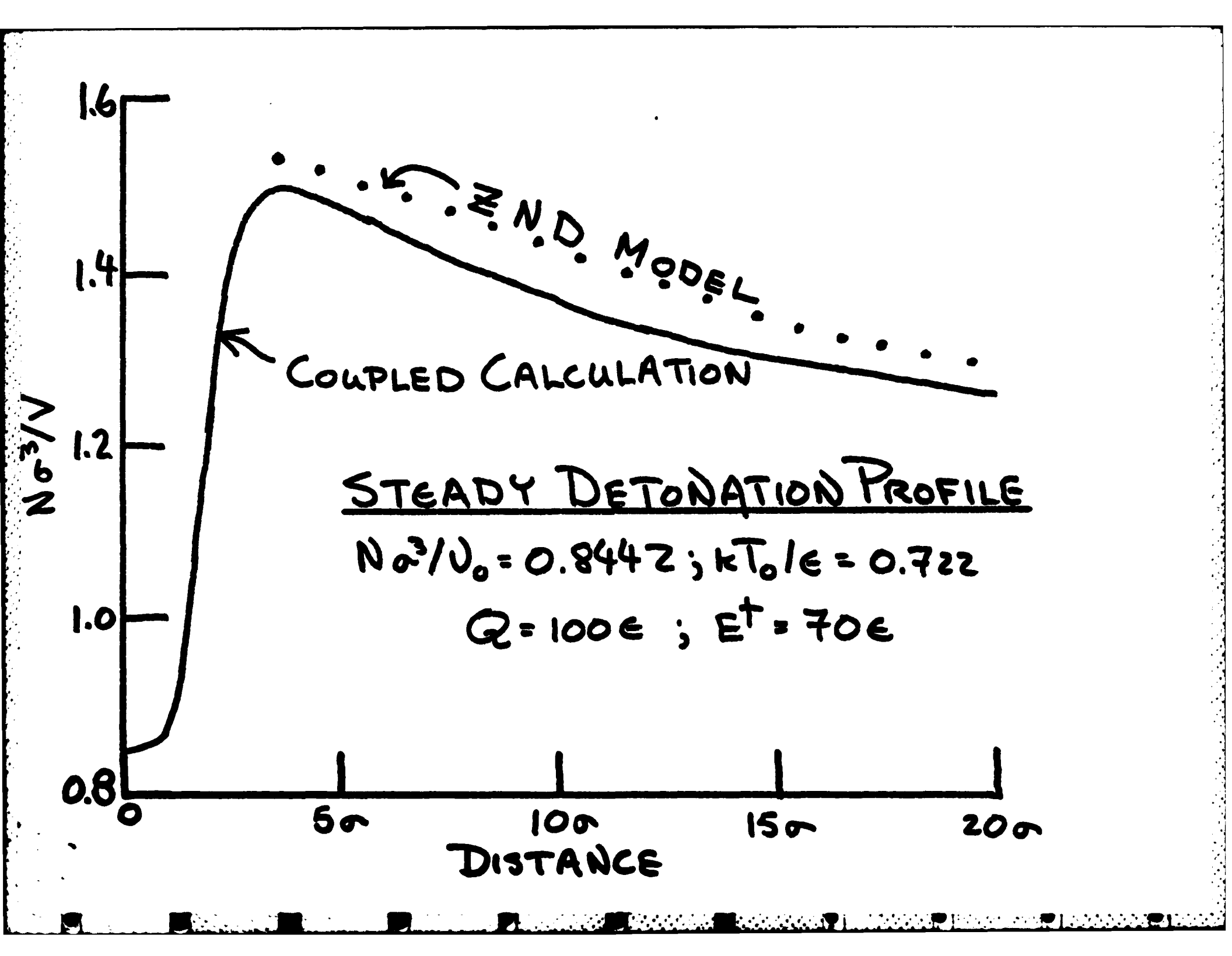

DIATOMIC LENNARD-JONE
DETONATION HUGONIOTS
$N\sigma^3/V_0 = 0.8442$
$kT_0/\epsilon = 0.722$
$P\sigma^3/\epsilon$
360
320
280
240
200
160
120
80
40
0
S
S
PRODUCTS Q=12.5ε
CJ
PRODUCTS Q=5.0ε
CJ
REACTANTS
0
0.6
0.7
0.8
0.9
1.0
1.1
1.2
$V/N\sigma$

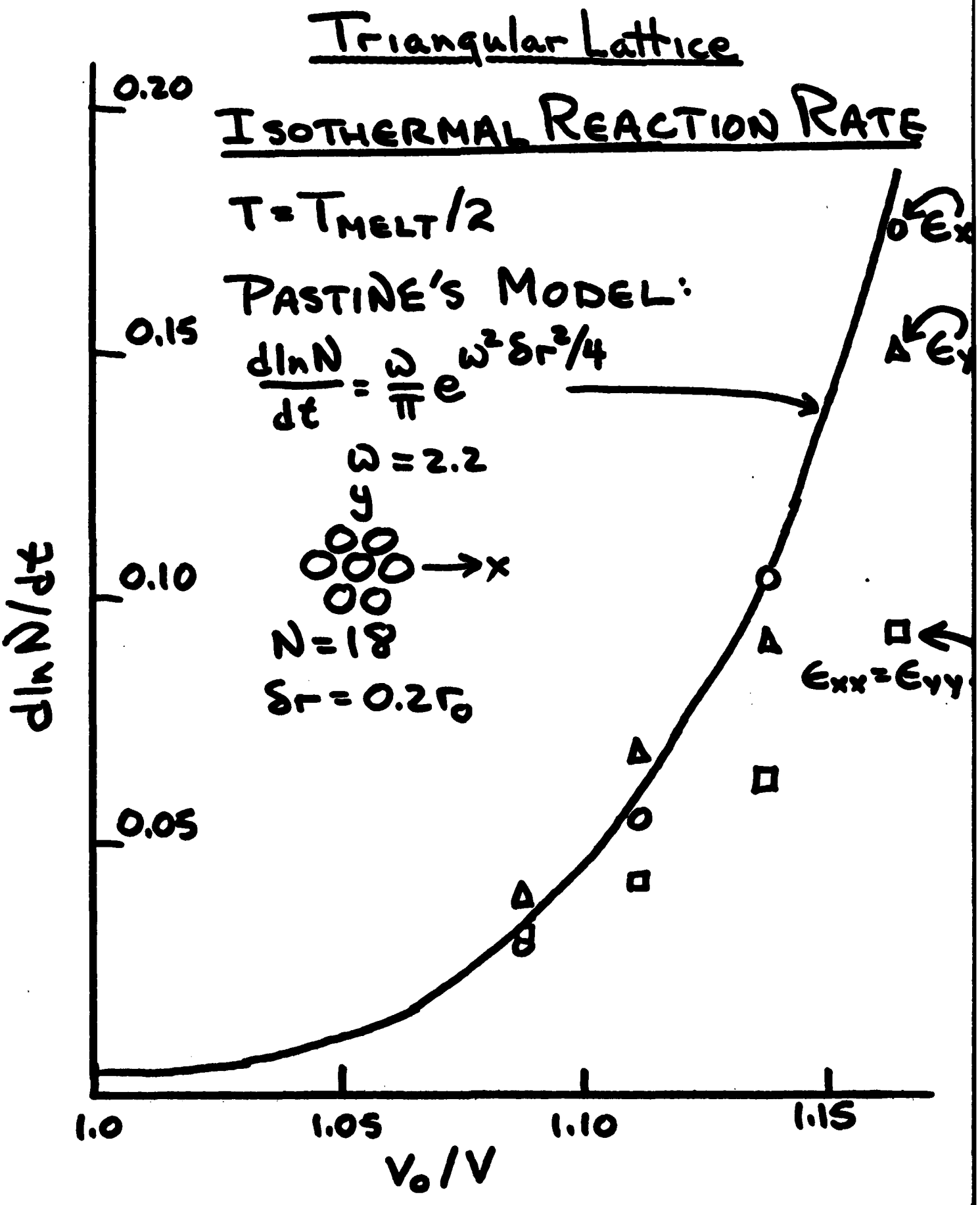
Figure 2

MONATOMIC LENNARD-JONES SHOCK WAVE PROFILES (SEE REF. 5)




1.6
1.4
1.2
1.0
0.8
$N\sigma^3/V$
Z.N.D. MODEL
COUPLED CALCULATION
STEADY DETONATION PROFILE
$N\sigma^3/V_0 = 0.8442$; $kT_0/\epsilon = 0.722$
$Q = 100\epsilon$; $E^t = 70\epsilon$
0
5σ
10σ
15σ
20σ
DISTANCE

Figure


Triangular Lattice
Isothermal Reaction Rate
T = T_MELT/2
Pastine's Model:
dlnN/dt = (ω/π) e^(ω²δr²/4)
ω = 2.2
N = 18
δr = 0.2r₀
0.20
0.15
0.10
0.05
dlnN/dt
1.0
1.05
1.10
1.15
V₀/V
ε_xx
ε_yy
ε_xx = ε_yy

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We are investigating mathematical models of detonation in dense fluids and in solids. We wish to obtain a fundamental understanding of the interaction of pressure waves, or shockwaves, with high explosives. We are solving the steady-state dynamical equations of continuum mechanics, including viscosity, conductivity, and chemical reactions, to simulate detonation in fluids capable of undergoing fast exothermic reactions. We are solving the coupled ordinary differential equations of motion of molecular dynamics, for solids, to simulate the initiation

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